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(54) Glazing panel having solar screening properties

(57) A glazing panel comprises a vitreous substrate carrying a pyrolytically formed tin/antimony oxide coating layer containing tin and antimony in a Sb/Sn molar ratio of from 0.01 to 0.5. The coated substrate has a solar factor FS of less than 70%. The panel is formed by chemical vapour deposition from a reactant mixture comprising a source of tin and a source of antimony. An intermediate haze-reducing coating layer of silicon oxide may be positioned between the substrate and the tin/antimony oxide coating layer.

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A GLAZING PANEL HAVING SOLAR SCREENING PROPERTIES
AND A PROCESS FOR MAKING SUCH A PANEL

The present invention relates to a glazing panel having solar screening properties and to a process for making such a panel.

Reflective transparent solar control glazing panels have become a useful material for architects to use for the exterior facade of buildings. Such panels have aesthetic qualities in reflecting the immediate environment and, being available in a number of colours, in providing a design opportunity. Such panels also have technical advantages by providing the occupants of a building with protection against solar radiation by reflection and/or absorption and eliminating the dazzling effects of intense sunshine, giving an effective screen against glare, enhancing visual comfort and reducing eye fatigue.

From a technical point of view, it is desired that the glazing panel shall not pass too great a proportion of total incident solar radiation in order that the interior of the building shall not become overheated in sunny weather. The transmission of total incident solar radiation may be expressed in terms of the "solar factor". As used herein, the term "solar factor" means the sum of the total energy directly transmitted and the energy which is absorbed and re-radiated on the side away from the energy source, as a proportion of the total radiant energy incident of the coated glass.

Another important application of reflective transparent solar control glazing panels is in vehicle windows, especially for motor cars or railway carriages, where the objective is to protect the vehicle occupants against solar radiation. In this case the main energy factor to be considered is the total energy directly transmitted (TE), since the energy

which is internally absorbed and re-radiated (AE) is dissipated by the movement of the vehicle. The essential aim of the vehicle panel is thus to have a low TE factor.

5 The properties of the coated substrate discussed herein are based on the standard definitions of the International Commission on Illumination - *Commission Internationale de l'Eclairage* ("CIE").

10 The standard illuminants quoted herein are CIE Illuminant C and Illuminant A. Illuminant C represents average daylight having a colour temperature of 6700°K. Illuminant A represents the radiation of a Planck radiator at a temperature of about 2856°K.

15 The "luminous transmittance" (TL) is the luminous flux transmitted through a substrate as a percentage of the incident luminous flux.

The "luminous reflectance" (RL) is the luminous flux reflected from a substrate as a percentage of the incident luminous flux.

20 The "selectivity" of a coated substrate for use in a building glazing panel is the ratio of the luminous transmittance to the solar factor (TL/FS).

25 The "purity" (p) of the colour of the substrate refers to the excitation purity measured with Illuminant C. It is specified according to a linear scale on which a defined white light source has a purity of zero and the pure colour has a purity of 100%. The purity of the coated substrate is measured from the side opposite the coated side.

The term "refractive index" (n) is defined in the CIE International Lighting Vocabulary, 1987, page 138.

The "dominant wavelength" (λ_0) is the peak wavelength in the range transmitted or reflected by the coated substrate.

The "emissivity" (ϵ) is the ratio of the energy emitted by a given surface at a given temperature to that of a perfect emitter (black body with emissivity of 1.0) at the same temperature.

A number of techniques are known for forming coatings on a vitreous substrate, including pyrolysis. Pyrolysis generally has the advantage of producing a hard coating, which precludes the need for a protective layer. The coatings formed by pyrolysis have durable abrasive- and corrosion-resistant properties. It is believed that this is due in particular to the fact the process involves depositing of coating material onto a substrate which is hot. Pyrolysis is also generally cheaper than alternative coating processes such as sputtering, particularly in terms of the investment in plant. The deposit of coatings by other processes, for example by sputtering, led to products with very different properties, in particular a lower resistance to abrasion and occasionally a different refractive index.

A wide variety of coating materials have been proposed for glazing panels, and for several different desired properties of the glazing. Tin oxide, SnO_2 , has been widely used, often in combination with other materials such as other metal oxides.

GB patent 1455148 teaches a method for pyrolytically forming a coating of one or more oxides on a substrate, primarily by spraying compounds of a metal or silicon, so as to modify the light transmission and/or light reflection of the substrate, or to impart antistatic or electrically conductive properties. Its examples of specified oxides include ZrO_2 , SnO_2 , Sb_2O_3 , TiO_2 , Co_3O_4 , Cr_2O_3 , SiO_2 and mixtures thereof. Tin

oxide (SnO_2) is seen as advantageous because of its hardness and its ability to have antistatic or electrically conductive properties. GB patent 2078213 relates to a sequential spray method for pyrolytically forming a coating on a vitreous support and is particularly concerned with tin oxide or indium oxide as the main coating constituents. When its metal coating precursor is tin chloride this is advantageously doped with a precursor selected from ammonium bifluoride and antimony chloride in order to increase the electrical conductivity of the coating.

It is also known that where a coating of tin oxide is formed by pyrolysis of SnCl_4 , the presence of a dopant such as antimony chloride SbCl_3 , directly mixed with the tin chloride SnCl_4 , improves the absorption and reflection of some near solar infrared radiation.

It is an object of the present invention to provide a pyrolytically formed glazing panel having solar screening properties.

We have discovered that this and other useful objectives can be achieved by utilising chemical vapour deposition (CVD) to apply a pyrolytic coating comprising tin and antimony oxides in a specific relative ratio.

Thus, according to a first aspect of the present invention, there is provided a glazing panel comprising a vitreous substrate carrying a tin/antimony oxide coating layer containing tin and antimony in a Sb/Sn molar ratio of from 0.01 to 0.5, the said coating layer having been pyrolytically formed by chemical vapour deposition, whereby the so-coated substrate has a solar factor FS of less than 70%.

The substrate is preferably in the form of a ribbon of vitreous material, such as glass or some other transparent rigid material. In view of the proportion of incident solar

radiation which is absorbed by the glazing panel, especially in environments where the panel is exposed to strong or long-term solar radiation, there is a heating effect on the glass panel which may require that the glass substrate be subsequently subjected to a toughening process. However, the durability of the coating enables the glazing panel to be mounted with the coated face outermost, thus reducing the heating effect.

Preferably, the substrate is clear glass, although the invention also extends to the use of coloured glass as the substrate.

The Sb/Sn molar ratio in the coating layer is preferably at least 0.03, most preferably at least 0.05. This assists in ensuring a high level of absorption. On the other hand the said ratio is preferably less than 0.21, with a view to achieving a high level of luminous transmittance (TL). Most preferably the ratio is less than 0.15, since above this level the coating layer displays an unduly high level of absorption, coupled with poor selectivity.

Coated substrates according to the invention offer the advantage of a luminous reflectance (RL) of less than 11%. This low level of reflection in a building glazing panel is much favoured by architects. It avoids the panels creating glare in the vicinity of the building.

It may be useful to prevent interaction between the glass of the substrate and the tin/antimony oxide coating layer. As an example, it has been found that in the pyrolytic formation of a tin oxide coating from tin chloride on a soda-lime glass substrate, sodium chloride tends to become incorporated into the coating as a result of reaction of the glass with the coating precursor material or its reaction products, and this leads to haze in the coating.

Thus, an intermediate haze-reducing coating layer is preferably positioned between the substrate and the tin/antimony oxide coating layer. The haze-reducing layer may be pyrolytically formed in an incompletely oxidized state by contacting the substrate in an undercoating chamber with undercoat precursor material in the presence of oxygen in insufficient quantity for full oxidation of the undercoat material on the substrate. The expression "incompletely oxidized material" is used herein to denote a true sub-oxide, that is to say an oxide of a lower valency state of a multivalent element (for example VO_2 or TiO), and also to denote an oxide material which contains oxygen gaps in its structure: an example of the latter material is SiO_x where x is less than 2, which may have the general structure of SiO_2 but has a proportion of gaps which would be filled with oxygen in the dioxide.

We prefer the haze-reducing coating layer to comprise a silicon oxide having a geometric thickness such as about 100 nm. The presence of a silicon oxide undercoating on soda-lime glass has the particular benefit of inhibiting the migration of sodium ions from the glass whether by diffusion or otherwise into the tin/antimony oxide coating layer either during formation of that upper layer or during a subsequent high temperature treatment.

Alternatively, the undercoat may be constituted as an "anti-reflection" undercoating such as, for example, an oxidised aluminium/vanadium layer as described in GB patent specification 2248243.

The glazing panels according to the invention have a solar factor of less than 70%, preferably less than 60% and in some instances preferably less than 50%. The preference for a solar factor of less than 60% arises when the panels according to the invention are positioned with the coated

side facing the exterior, i.e. facing the energy source.

Generally, this positioning leads to a improved solar factor compared with the positioning of the panel with the coated side away from the energy source. The need for a solar

5 factor of less than 50% arises for buildings in parts of the world with high levels of solar energy. For vehicle sunroofs an even lower solar factor may be desirable.

The use of coloured glass is one way of providing a lower solar factor, and is commonly employed in both building glass
10 and vehicle glass. In comparing the effectiveness of coating layers it is therefore necessary to take into account any differences between the types of glass on which the respective coatings are deposited. Thus one example of a coating according to the invention on clear glass gave a
15 solar factor of 63%, whereas an equivalent coating on a green coloured glass gave a solar factor of 44.5%.

It is also desired that the glazing panel shall also transmit a reasonable proportion of visible light in order to allow natural illumination of the interior of the building or
20 vehicle and in order to allow its occupants to see out. Thus it is desirable to increase the selectivity of the coating, that is to increase the ratio of the transmittance to the solar factor. Indeed it is preferred that the selectivity be as high as possible.

25 In general it is preferred that the luminous transmittance (TL) of the panel according to the invention is between 40 and 65%. Nevertheless, a panel having a light transmittance below 40% may be used as a roofing panel, for example as a vehicle sunroof.

30 Preferably, the tin/antimony oxide coating has a thickness of from 100 to 500 nm. Thick layers of tin/antimony oxide, particularly layers having a low Sb/Sn molar ratio, can provide a glazing panel with the advantageous combination of

a low solar factor (FS) and low emissivity. Another way of obtaining this combination is to deposit on the tin/antimony oxide layer of the invention a low-emissivity layer of doped tin oxide, for example tin oxide doped with fluorine. However this is disadvantageous in the sense that it makes necessary the deposition of a supplementary layer, which is time-consuming and expensive.

In principle, another way to provide a combination of low solar factor and low emissivity could be to form a tin/antimony oxide layer containing a doping agent such as fluorine. For example GB patent 2200139 teaches a method of forming a pyrolytic tin oxide coating by spraying a solution which in addition to the tin precursor contains compounds which will result in the coating containing fluorine and at least one of antimony, arsenic, vanadium, cobalt, zinc, cadmium, tungsten, tellurium and manganese.

Thus one could, for instance, form a coating from reactants containing tin, antimony and fluorine in the ratios $Sb/Sn = 0.028$, $F/Sn = 0.04$. However we have discovered that the presence of fluorine has the apparent disadvantage of hindering the incorporation of antimony in the coating rather than effectively reducing the emissivity. For example reactants containing antimony and tin in the ratio $Sb/Sn = 0.028$ gave a coating with an Sb/Sn ratio of about 0.057, whilst the same reactants plus a fluorine-containing reactant in an amount such that $F/Sn = 0.04$ gave a coating with an Sb/Sn ratio of about 0.038.

The invention accordingly presents the advantage of simultaneously providing a solar factor (FS) below 60%, an emissivity of less than 0.4 (preferably less than 0.3) and a luminous transmittance (TL) of more than 60%. Thus the coated product fulfils two important functions. In winter it maintains the heat in the building, because of its low

emissivity. In summer it resists the passage of solar heat into the building and thus avoids overheating inside the building, thanks to its low solar factor. This is especially achieved for coatings having an Sb/Sn ratio between 0.01 and 0.12, especially 0.03 to 0.07, and a thickness between 100 and 500 nm, for example between 250 and 450 nm.

Preferably the tin/antimony oxide coating layer is an exposed coating layer and the glazed panel comprises only one such tin/antimony oxide coating layer.

However, it is possible to provide one or more further coating layers, whether by pyrolysis or by other coating methods, to achieve certain desired optical qualities. It should be noted however, that the tin/antimony oxide layer when applied by pyrolysis has sufficient mechanical durability and chemical resistance to suitably serve as the exposed layer.

The panels according to the invention may be installed in single or multi-glazed assemblies. While the coated surface of the panel may be the inside surface of the exterior glazing panel so that the coated surface is not exposed to the ambient weather conditions which might otherwise more rapidly reduce its life by soiling, physical damage and/or oxidation, coatings produced by pyrolysis generally have a greater mechanical resistance than coatings produced by other methods and they may therefore be exposed to the atmosphere.

The panels according to the invention may usefully be employed in laminated glass structures, for example where the coated surface is the inside surface of the exterior laminate.

According to a second aspect of the invention, there is provided a process of forming a glazing panel comprising the chemical vapour deposition of a tin/antimony oxide layer from a reactant mixture on to a vitreous substrate, said reactant

mixture comprising a source of tin and a source of antimony, the Sb/Sn molar ratio in said mixture being from 0.01 to 0.5, whereby the so-coated substrate has a solar factor FS of less than 70%.

5 When it is desired to manufacture pyrolytically coated flat glass, it is best to do so when the glass is newly formed. To do so has economic benefits in that there is no need to reheat the glass for the pyrolytic reactions to take place, and it also has benefits as to the quality of the coating,
10 since it is assured that the surface of the glass is in pristine condition. Preferably, therefore, said undercoat precursor material is brought into contact with an upper face of a hot glass substrate constituted by freshly-formed flat glass.

15 Thus, the glazing panels according to the invention may be manufactured as follows. Each pyrolytic coating step may be carried out at a temperature of at least 400°C, ideally from 550°C to 750°C. The coatings can be formed on a sheet of glass which moves in a tunnel oven or on a glass ribbon
20 during formation, whilst it is still hot. The coatings can be formed inside thelehr which follows the glass ribbon forming device or inside the float tank on the top face of the glass ribbon whilst the latter is floating on a bath of molten tin.

25 The coating layers are applied to the substrate by chemical vapour deposition (CVD). This is a particularly beneficial method because it provides for coatings of regular thickness and composition, such uniformity of the coating being particularly important where the product is to cover a larg
30 area. CVD offers many advantages over pyrolysis methods using sprayed liquids as the reactant materials. With such spray methods it is difficult both to control the vaporisation process and to obtain a good uniformity of

coating thickness. Moreover, the pyrolysis of sprayed liquids is essentially limited to the manufacture of oxide coatings, such as SnO_2 and TiO_2 . It is also difficult to make multi-layer coatings using sprayed liquids because every coating deposition produces a significant cooling of the substrate. Furthermore, chemical vapour deposition is more economic in terms of raw materials, leading to lower wastage.

The product with a CVD coating is physically different from those with coatings obtained by spraying. Notably a spray coating retains traces of the sprayed droplets and of the path of the spray gun, which is not the case with CVD.

To form each coating, the substrate is brought into contact, in a coating chamber, with a gaseous medium comprising the reactant mixture in the gaseous phase. The coating chamber is fed with the reactant gas through one or more nozzles, the length of which is at least equal to the width to be coated.

Methods and devices for forming such a coating are described for example in French patent No 2 348 166 (BFG Glassgroup) or in French patent application No 2 648 453 A1 (Glaverbel). These methods and devices lead to the formation of particularly strong coatings with advantageous optical properties.

To form the coatings of tin/antimony oxide, two successive nozzles are used. The reactant mixture comprising the sources of tin and antimony are fed in at the first nozzle. Where this mixture comprises chlorides which are liquid at ambient temperature, it is vaporised in a current of anhydrous carrier gas at an elevated temperature. Vaporisation is facilitated by the atomization of these reagents in the carrier gas. To produce the oxides, the chlorides are brought into the presence of water vapour conducted to the second nozzle. The water vapour is superheated and is also injected into a carrier gas.

Advantageously, nitrogen is used as the substantially inert carrier gas. Nitrogen is sufficiently inert for the purposes in view, and it is inexpensive when compared with the noble gases.

- 5 Undercoatings of silicon oxide SiO_2 or SiO_x may be deposited from silane SiH_4 and oxygen in accordance with the descriptions in British patent specifications GB 2234264 and GB 2247691.

10 If a glass substrate bearing an incompletely oxidized coating is exposed to an oxidizing atmosphere for a sufficiently long period of time, it may be expected that the coating will tend to become fully oxidized so that its desired properties are lost. Therefore, such undercoat is over-coated with the tin/antimony oxide coating layer while it is still in an
15 incompletely oxidized state, and while the substrate is still hot, thereby to preserve such undercoat in an incompletely oxidized state. The time during which the freshly undercoated glass substrate may be exposed to an oxidizing atmosphere such as air and before the undercoat is over-
20 coated, without damaging the properties of the undercoat, will depend on the temperature of the glass during such exposure and on the nature of the undercoat.

Advantageously, said undercoating chamber is surrounded by a reducing atmosphere. The adoption of this feature assists
25 in preventing ambient oxygen from entering the undercoating chamber and accordingly allows better control of the oxidizing conditions within that undercoating chamber.

The oxygen required for the undercoating reactions may be supplied as pure oxygen, but this adds unnecessarily to
30 costs, and it is accordingly preferred that air is supplied to the undercoating chamber in order to introduce oxygen thereto.

It will be noted that the Sb/Sn molar ratio which is desirable in the reactant mixture does not always correspond to that ratio which is desirable for the tin/antimony coating layer

- 5 Preferably the source of tin is selected from SnCl_4 , monobutyl trichloro tin ("MBTC") and mixtures thereof. The source of antimony may be selected from SbCl_5 , SbCl_3 , organo antimony compounds and mixtures thereof. Examples of suitable source materials are $\text{Sb}(\text{OCH}_2\text{CH}_3)_3$, $\text{Cl}_{1.7}\text{Sb}(\text{OCH}_2\text{CH}_3)_{1.3}$, $\text{Cl}_2\text{SbOCHClCH}_3$, $\text{Cl}_2\text{SbOCH}_2\text{CHCH}_3\text{Cl}$ and $\text{Cl}_2\text{SbOCH}_2\text{C}(\text{CH}_3)_2\text{Cl}$.
- 10

The invention will now be described in more detail, with reference to the following non-limiting examples.

- In the Examples the Sb/Sn molar ratio in the coating layers was determined by an X-ray analysis technique in which the number of X-ray counts of the respective elements was compared. While this technique is not as precise as if a calibration by chemical dosage were made, the similarity of antimony and tin means that they respond similarly to X-rays.
- 15

- The ratio of the measured number of observed counts of the respective elements thus provides a close approximation to their molar ratio.
- 20

- Coloured rather than clear glass was employed as indicated in some of the Examples. The properties of the respective types of coloured glass are shown in Table 1 below. In all cases the properties were measured on glass samples having a thickness of 4 mm, this being the thickness of glass employed in all the examples except Examples 1 to 7 (for which the thicknesses are shown in Table 2). The initials in the headings to this and the other following tables (TL, TE etc.) have the meanings described above.
- 25
- 30

With regard to the calculation of the solar factor, it should be noted that for luminous transmittances (TL) below

60% the effect of low emissivity is not negligible and should be taken into account: as the emissivity reduces so equally does the solar factor.

Table 1

| <u>Glass Type</u> | Green A | Green B | Grey | Medium Grey | Dark Grey |
|---|-------------|-------------|-------------|-------------|-------------|
| λ D in transmission (nm) [Illuminant: C/A] | 505.4/508.5 | 504.9/508.4 | 470.1/493.9 | 493.2/502.7 | 478.9/502.7 |
| Purity (%) | 2.9/3.4 | 2.1/2.5 | 1.5/0.8 | 5.6/5.1 | 2.6/1.8 |
| TL (%) [Illuminant: C/A] | 72.66/71.12 | 78.44/77.20 | 55.65/55.56 | 36.80/35.76 | 22.41/22.30 |
| TE (%) (CIE) | 44.0 | 52.3 | 56.9 | 25.9 | 31.11 |
| FS (%) coated side (CIE) | 56.8 | 62.9 | 66.3 | 43.4 | 47.3 |
| TL/FS [Illuminant: C] | 1.28 | 1.25 | 0.84 | 0.85 | 0.47 |

5

Example 1

Clear soda-lime float glass advancing at a speed of 7 metres per minute along a float chamber was undercoated at a coating station located at a position along the float chamber where the glass was at a temperature of about 700°C. The supply line was fed with nitrogen, silane was introduced thereto with a partial pressure of 0.25%, and oxygen was introduced with a partial pressure of 0.5% (ratio 0.5). A coating of silicon oxide SiO₂ having a thickness of 100 nm was obtained.

10

15

The undercoated substrate, having a thickness of 6 mm was then immediately coated by CVD pyrolysis using a coating apparatus comprising two successive nozzles. A reagent comprising a mixture of SnCl₄ as a source of tin and SbCl₃ as

a source of antimony was used. The Sb/Sn molar ratio in the mixture was about 0.2. The reactant mixture was vaporised in a current of anhydrous nitrogen gas at about 600°C, was fed in at the first nozzle. Vaporisation was facilitated by the atomization of these reagents in the carrier gas.

Superheated water vapour was conducted to the second nozzle.

The water vapour was heated to about 600°C, and was also injected into a carrier gas, which was air heated to about 600°C. The flow rate of gas (carrier gas + reagent) in each nozzle was 1 m³/cm width of substrate per hour, at the operating temperature.

The coating process was continued until the geometrical thickness of the tin/antimony oxide coating superimposed on the undercoated substrate was 185 nm.

Examples 2 to 7

In Examples 2 to 7, the procedure of Example 1 was followed but with variations in such parameters as the reactant mixture, the presence or absence of an undercoat oxide, the ratio of Sb/Sn in the coating and in the reactant mixture and the thickness of the glass substrate. For instance, compared with Example 1, in Example 2 no undercoating was applied and the tin/antimony oxide coating layer had a thickness of 210 nm. The reactant mixtures were as follows:

Examples 2 and 3: the same as in Example 1 (but with a lower concentration of the reactant mixture in the carrier gas in Example 3);

Example 4: MBTC and Cl_{1.7}Sb(OCH₂CH₃)_{1.3}; [cf. GVB ST/171 p3!]

Example 5: MBTC and Cl₂SbOCH₂CHCH₃Cl;

Example 6: MBTC and Cl₂SbOCH₂C(CH₃)₂Cl;

Example 7: MBTC and SbCl_3 .

The variations in operating parameters for Examples 1 to 7 and the results obtained are given in the accompanying Table 2.

- 5 The glazing panels according to Examples 3 to 7 had a pleasant blue colour in transmission: the dominant wavelength in transmission in the visible wavelength lay within the range of 470 to 490 nm.

10 Example 6 provided a glazing panel with the combination of a low solar factor FS and low emissivity.

In a variant of Example 6 the SiO_2 undercoating was replaced by an anti-reflection undercoating of silicon oxide SiO_x according to the procedure of GB patent 2247691. In another variant the SiO_2 undercoating was replaced by an oxidised
15 aluminium/vanadium layer according to GB patent 2248243. In these variants the glazing panel had no purple aspect in the reflection from the uncoated side.

Example 8

Coloured float glass "Green A" advancing at a speed of 7
20 metres per minute along a float chamber was undercoated at a coating station located at a position along the float chamber where the glass was at a temperature of about 700°C . The supply line was fed with nitrogen, silane was introduced thereto with a partial pressure of 0.2%, and oxygen was
25 introduced with a partial pressure of 0.5% (ratio 0.55). A coating of silicon oxide SiO_x , with x approximately equal to 1.8, was obtained with a refractive index of about 1.7. The thickness of the coating was 40 nm.

30 Th undercoated substrate, having a thickness of 4 mm, was then coated by CVD pyrolysis. A reagent comprising a mixture of MBTC as a source of tin and $\text{Cl}_{1.7}\text{Sb}(\text{OCH}_2\text{CH}_3)_{1.3}$ as a

source of antimony was used. The Sb/Sn molar ratio in the mixture was about 0.195 (mass ratio 0.2). The reactant mixture was vaporised in a current of anhydrous air at about 200°C, fed in at the nozzle. Vaporisation was facilitated by the atomization of these reagents in the carrier gas. Superheated water vapour was then introduced, heated to about 200°C.

The coating process was continued until the geometrical thickness of the tin/antimony oxide coating superimposed on the undercoated substrate was 120 nm.

Examples 9 to 14

In Examples 9 to 14, the procedure of Example 8 was followed but with variations as shown in the accompanying Table 2 in such parameters as the thickness of the undercoat, the ratio of Sb/Sn in the coating and in the reaction mixture, the thickness of the tin/antimony oxide coating layer and the colour of the glass. The results of examples 8 to 14 are set out in Table 3.

The glazing panels according to the Examples 9 to 14 had a pleasant blue colour in transmission, the dominant wavelength in transmission in the visible wavelength lying within the range of 470 to 490 nm (Illuminant C).

In a variant of Example 9 in which the Green A glass was replaced by Medium Grey glass, the resultant luminous transmittance (TL) was 20%, the luminous reflectance (RL) was 10% and the energy transmission (TE) was 15 %.

Examples 15 to 30

The procedure of Example 1 was followed for further Examples 15 to 30 with variations in the reactant mixture, the colour and thickness of the glass substrate, the thickness of undercoat oxide, and the ratio of Sb/Sn in the reactant

mixture and in the coating and in the reaction mixture. For Examples 15 to 22 the reactant mixture was MBTC and $\text{Cl}_{1.7}\text{Sb}(\text{OCH}_2\text{CH}_3)_{1.3}$ without trifluoroacetic acid whereas for Examples 23 to 30 the reactant mixture was MBTC and $\text{Cl}_{1.7}\text{Sb}(\text{OCH}_2\text{CH}_3)_{1.3}$ with trifluoroacetic acid. The F/Sn ratio in the reactant mixture for these examples was 0.04.

The variations in operating parameters, and the results obtained, are set out in the accompanying Table 4 for Examples 15 to 22 and in the accompanying Table 5 for Examples 23 to 30. The silicon oxide SiO_x used in Examples 15 to 30 had a value of x approximately equal to 1.8.

Table 2

| Example | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|------------------|--------|--------------|------------------|------------------|------------------|------------------|
| Tin/antimony oxide thickness (nm) | 185 | 210 | 105 | 120 | 105 | 445 | 110 |
| Undercoat oxide | SiO ₂ | absent | absent | SiO ₂ | SiO ₂ | SiO ₂ | SiO ₂ |
| Undercoat thickness (nm) | 100 | 0 | 0 | 70 | 70 | 70 | 70 |
| Sb/Sn ratio in coating | 0.48 | 0.48 | 0.46 | 0.19 | 0.15 | 0.06 | 0.18 |
| Sb/Sn ratio in reactants | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.10 | 0.20 |
| Haze (%) | 0.07 | 2.09 | 4.36 to 7.01 | low | low | low | low |
| TL (%) | 45.7 | 44.3 | 65.5 | 51.0 | 61.6 | 47.5 | 55.0 |
| RL (%) (coated side) | 9.0 | 12.0 | 18.8 | 12.0 | 11.7 | 6.6 | 13.7 |
| FS (%) (coated side) (CIE) | 55.3 | 56.9 | 66.0 | 58.4 | 62.2 | 47.2 | 59.6 |
| TL/FS | 0.83 | 0.78 | 0.99 | 0.87 | 0.99 | 1.01 | 0.92 |
| λ_D in transmission (nm) | 587.5 | -560 | 480.1 | 478.8 | 481.0 | 483.0 | 479.3 |
| Colour purity in transmission (%) | 3.4 | 3.9 | 4.9 | 11.5 | 8.7 | 8.0 | 10.3 |
| λ_D in reflection from the coated side (nm) | 472.3 | 494.5 | 575.3 | 579.5 | 577.6 | 490.0 | 577.0 |
| Colour purity (%) in reflection from the coated side | 36.9 | 7.0 | 19.1 | 35.0 | 35.2 | 6.0 | 33.1 |
| Emissivity | >0.7 | >0.7 | >0.7 | 0.84 | 0.71 | 0.25 | 0.79 |
| Glass thickness (mm) | 6 | 6 | 6 | 5 | 5 | 5 | 5 |

Table 3

| Example | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|--|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Tin/antimony oxide thickness (nm) | 120 | 120 | 320 | 470 | 470 | 320 | 470 |
| Undercoat oxide | SiO ₂ | SiO ₂ | SiO ₂ | SiO ₂ | SiO ₂ | SiO ₂ | SiO ₂ |
| Undercoat thickness (nm) | 40 | 70 | 40 | 40 | 40 | 40 | 40 |
| Sb/Sn ratio in coating | 0.10 | 0.18 | 0.09 | 0.09 | 0.09 | 0.09 | 0.09 |
| Sb/Sn ratio in reactants | 0.07 | 0.20 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 |
| Haze (%) | 0.36 | 0.1 | 1.0 | 1.8 | 1.8 | 1.0 | 1.8 |
| TL (%) [Illuminant A/Illuminant C] | 53/55 | 39/20 | 31/32 | 31/32 | 9/9 | 40/41 | 36 [A] |
| RL (%) (coated side) [Illuminant A/C] | 9/10 | 11/11 | 7/7 | 7/7 | 7/7 | 8/7 | 7 [A] |
| RL (%) (uncoated side) [Illuminant C] | 8 | 8 | 6 | 6 | 5 | 7 | - |
| TE (%) (CIE) | 31 | 25 | 25 | 18 | 9 | 21 | 27 |
| FS (%) (coated side) (CIE) | 45 | 41 | 41 | 36 | 29 | 39 | 43 |
| TL/FS | 1.2/1.2 | 0.95/0.98 | 0.76/0.78 | 0.86/0.89 | 0.31/0.31 | 1.02/1.05 | 5.4 [A] |
| λ_D in transmission (nm) | 505.5/498.6 | 497.2/487.0 | 494.8/481.9 | 497.2/487.2 | 494.2/480.0 | 501.0/491.6 | 493.4 [A] |
| Colour purity in transmission (%) | 4.4/4.2 | 6.2/8.9 | 4.9/8.1 | 7.6/10.8 | 7.0/11.8 | 7.2/8.6 | 5.4 [A] |
| λ_D in reflection from the coated side (nm) | 487.9/478.1 | -572.5/566.9 | -511.8/512.2 | -576.9/559.8 | -555.4/550.1 | -512.5/513.6 | -576.0 [A] |
| Colour purity (%) in reflection from the coated side | 7.4/14.6 | 2.2/2.9 | 17.2/16.3 | 6.0/1.2 | 2.1/6.6 | 15.4/14.5 | 1.5 [A] |
| Emissivity | 0.71 | 0.85 | 0.44 | 0.35 | 0.35 | 0.44 | 0.35 |
| Colour of glass | Green A | Green A | Grey | Green B | Dark grey | Green A | Clear soda lime |

Table 4

| Example | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|---|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Tin/antimony oxide thickness (nm) | 320 | 320 | 320 | 320 | 390 | 390 | 390 | 390 |
| Undercoat oxide | SiO _x | SiO _x | SiO _x | SiO _x | SiO _x | SiO _x | SiO _x | SiO _x |
| Undercoat thickness (nm) | 60 (approx) | 60 (approx) | 60 (approx) | 60 (approx) | 80 (approx) | 80 (approx) | 80 (approx) | 80 (approx) |
| Sb/Sn ratio in coating | 0.053 | 0.053 | 0.053 | 0.053 | 0.058 | 0.058 | 0.058 | 0.058 |
| Sb/Sn ratio in reactants | 0.028 | 0.028 | 0.028 | 0.028 | 0.028 | 0.028 | 0.028 | 0.028 |
| Haze (%) | 0.65 | 0.65 | 0.65 | 0.65 | 1.2 | 1.2 | 1.2 | 1.2 |
| TL (%) [Illuminant C] | 68.8 | 55.7 | 60.1 | 28.2 | 61.0 | 49.2 | 25.0 | 53.1 |
| RL (%) (coated side) | 8.9 | 8.2 | 8.4 | 7.2 | 9.0 | 8.0 | 7.2 | 6.9 |
| RL (%) (uncoated side) | 8.9 | 7.3 | 7.8 | 5.0 | 7.8 | 6.5 | 4.8 | 8.2 |
| TE (%) (CIE) | 50.8 | 28.3 | 33.1 | 15.8 | 43.0 | 24.5 | 13.7 | 28.5 |
| FS (%) (coated side) (CIE) | 60.3 | 43.6 | 47.2 | 34.4 | 54.7 | 40.9 | 32.9 | 40.1 |
| TL/TE | 1.35 | 2.00 | 1.82 | 1.75 | 1.42 | 1.96 | 1.79 | 1.86 |
| TL/FS | 1.15 | 1.27 | 1.28 | 0.82 | 1.11 | 1.20 | 0.76 | 1.20 |
| λ_D in transmission (nm) | 524.0 | 506.2 | 506.0 | 494.0 | 496.0 | 500.7 | 493.4 | 499.5 |
| Colour purity in transmission (%) | 0.5 | 3.1 | 2.3 | 5.8 | 2.2 | 4.7 | 7.5 | 4.1 |
| λ_D in reflection from the coated side (nm) | 482.9 | 484.2 | 484.0 | 482.9 | 495.2 | 493.8 | 495.0 | 550.3 |
| C colour purity (%) in reflection from the coated side | 14.5 | 16.2 | 15.8 | 18.0 | 5.0 | 4.4 | 6.4 | 7.0 |
| Emissivity | 0.29 | 0.29 | 0.29 | 0.29 | 0.27 | 0.27 | 0.27 | 0.27 |
| Colour of glass | Clear | Green A | Green B | Med. grey | Clear | Green A | Med. grey | Green B |

Table 5

| Example | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
|---|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Tin/antimony oxide thickness (nm) | 290 | 290 | 290 | 290 | 410 | 410 | 410 | 410 |
| Undercoat oxide | SiO _x | SiO _x | SiO _x | SiO _x | SiO _x | SiO _x | SiO _x | SiO _x |
| Undercoat thickness (nm) | 80 (approx) | 80 (approx) | 80 (approx) | 80 (approx) | 90 (approx) | 90 (approx) | 90 (approx) | 90 (approx) |
| Sb/Sn ratio in coating | 0.038 | 0.038 | 0.038 | 0.038 | 0.037 | 0.037 | 0.037 | 0.037 |
| Sb/Sn ratio in reactants | 0.028 | 0.028 | 0.028 | 0.028 | 0.028 | 0.028 | 0.028 | 0.028 |
| Haze (%) | 0.82 | 0.82 | 0.82 | 0.82 | 1.2 | 1.2 | 1.2 | 1.2 |
| TL (%) [Illuminant C] | 70.2 | 56.7 | 61.0 | 28.7 | 64.2 | 51.9 | 26.9 | 56.4 |
| RL (%) (coated side) | 10.0 | 9.0 | 9.2 | 8.0 | 8.8 | 8.1 | 7.2 | 8.3 |
| RL (%) (uncoated side) | 9.5 | 8.0 | 8.3 | 5.2 | 7.7 | 6.6 | 4.8 | 6.9 |
| TE (%) (CIE) | 54.3 | 29.5 | 34.7 | 16.6 | 47.2 | 26.1 | 14.6 | 30.6 |
| FS (%) (coated side) (CIE) | 63.0 | 44.5 | 48.3 | 34.9 | 57.7 | 42.0 | 33.6 | 45.4 |
| TL/TE | 1.30 | 1.90 | 1.74 | 1.71 | 1.36 | 2.00 | 1.73 | 1.81 |
| TL/FS | 1.11 | 1.27 | 1.27 | 0.83 | 1.10 | 1.24 | 0.76 | 1.24 |
| λ_D in transmission (nm) | 581.3 | 538.8 | 549.4 | 498.5 | 568.6 | 535.9 | 502.7 | 543.7 |
| Colour purity in transmission (%) | 2.9 | 2.9 | 2.7 | 3.3 | 3.5 | 3.7 | 3.6 | 3.5 |
| λ_D in reflection from the coated side (nm) | 510.3 | 508.6 | 508.9 | 507.2 | 549.3 | 505.1 | 491.8 | 507.0 |
| Colour purity (%) in reflection from the coated side | 8.1 | 10.1 | 9.6 | 11.3 | 3.3 | 1.1 | 1.2 | 1.0 |
| Emissivity | 0.28 | 0.28 | 0.28 | 0.28 | 0.23 | 0.23 | 0.23 | 0.23 |
| Colour f glass | Clear | Green A | Green B | Med. grey | Clear | Green A | Med. grey | Green B |

CLAIMS

1. A glazing panel comprising a vitreous substrate carrying a tin/antimony oxide coating layer containing tin and antimony in a Sb/Sn molar ratio of from 0.01 to 0.5, the said coating layer
5 having been pyrolytically formed by chemical vapour deposition, whereby the so-coated substrate has a solar factor (FS) of less than 70%.
2. A glazing panel according to claim 1, wherein the Sb/Sn molar ratio is at least 0.03.
- 10 3. A glazing panel according to claim 2, wherein the Sb/Sn molar ratio is at least 0.05.
4. A glazing panel according to any preceding claim, wherein the Sb/Sn molar ratio is less than 0.21.
5. A glazing panel according to claim 1 or claim 4, wherein
15 the Sb/Sn molar ratio is between 0.01 and 0.12.
6. A glazing panel according to claim 5, wherein the Sb/Sn molar ratio is between 0.03 and 0.07.
7. A glazing panel according to any preceding claim, wherein an intermediate haze-reducing coating layer is positioned
20 between the substrate and the tin/antimony oxide coating layer.
8. A glazing panel according to claim 7, wherein the said haze-reducing coating layer comprises silicon oxide
9. A glazing panel according to any preceding claim, wherein the solar factor is less than 60%.
- 25 10. A glazing panel according to claim 9, wherein the solar factor is less than 50%.
11. A glazing panel according to any preceding claim, having a luminous transmittance (TL) of between 40 and 65%.

12. A glazing panel according to any preceding claim, wherein the said tin/antimony oxide coating has a thickness of from 100 to 500 nm.

13. A glazing panel according to claim 12, wherein the tin/antimony oxide coating has a thickness of from 250 to 450 nm.

14. A glazing panel according to any preceding claim, wherein the tin/antimony oxide coating layer is an exposed coating layer.

15. A glazing panel according to any preceding claim, comprising only one said tin/antimony oxide coating layer.

16. A process of forming a glazing panel comprising the chemical vapour deposition of a tin/antimony oxide layer from a reactant mixture onto a vitreous substrate, said reactant mixture comprising a source of tin and a source of antimony, the molar ratio of antimony to tin in said mixture being from 0.01 to 0.5, whereby the so-coated substrate has a solar factor (FS) of less than 70%.

17. A process according to claim 16, wherein the said source of tin is selected from SnCl_4 , monobutyl trichloro tin and mixtures thereof.

18. A process according to claim 16 or 17, wherein the source of antimony is selected from antimony chlorides, organo antimony compounds and mixtures thereof.



Applicati n N : GB 9611312.1
Claims searched: 1-18

Examiner: Peter Beddoe
Date of search: 25 July 1996

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.O): C7F (FHB,FHD,FHE,FHX)

Int CI (Ed.6): C03C (17/23,17/245,17/25); C23C 16/40

Other: Online: WPI, CLAIMS

Documents considered to be relevant:

| Category | Identity of document and relevant passage | Relevant to claims |
|----------|---|--------------------|
| X | GB 2078213 A (BFG) see esp ex 4 | 1,12-17 |
| X | GB 2044137 A (SOCIETA ITALIANA) see esp page 6 lines 17-29 | 1,12-17 |
| X | GB 1517341 (DAY) see esp table 1 | 1,12-17 |
| X | GB 866332 (PITTSBURGH) see esp page 6 lines 21-24 | 1,12-17 |
| X | US 5382383 (CATALYSTS) see esp col 5 line 52 - col 6 line 30 | 1,12-17 |
| X | US 4983261 (ASEA) see esp col 2 line 44-68 | 1,12-17 |
| X | US 4900634 (GLAVERBEL) see esp exs 1,3,4 | 1,12-17 |
| X | US 4873352 (EXLAN) see esp ex 3 | 1,12-17 |
| X | US 4859496 (MATSUSHITA) see esp col 5 (incl figs0 | 1,12-17 |
| X,P | WPI Accession no 96-263711/27 & JP 080109042 A (NIPPON) 30 April 1996, see abstract | 1,12-17 |
| X,P | WPI Accession no 96-205342/21 & JP 080073242 A (NIPPON) 19 March 1996, see abstract | 1,12-17 |

X Document indicating lack of novelty or inventive step
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A Document indicating technological background and/or state of the art.
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E Patent document published on or after, but with priority date earlier than, the filing date of this application.



The
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Application No: GB 9611312.1
Claims searched: 1-18

Examiner: Peter Beddoe
Date of search: 25 July 1996

| Category | Identity of document and relevant passage | Relevant to claims |
|----------|---|--------------------|
| X | WPI Accession no 91-169065/23 & JP 030103341 A (NIPPON) see abstract | 1,12-17 |
| X | WPI Accession no 79-69149B/38 & JP 540103414 A (SHIBARU) see abstract | 1,12-17 |

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E Patent document published on or after, but with priority date earlier than, the filing date of this application.

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